

2.6 Environmental Measurements



CSTL activities that support stewardship of the environment extend from the enhancement of industrial process efficiency for pollution prevention to the assessment and remediation of environmental problems through the development of measurements, data, models, and reference standards. CSTL has served as a partner to both industry and measurement laboratories for many years in dealing with environmental concerns by providing the tools needed for sustainable development and the shared goals of environmental protection and socio-economic growth. Environmental activities within CSTL fall under the broad categories of *Assessment* (identification and measurement of pollutants and monitoring of environmental health) and *Green Chemistry* (pollution prevention through the improvement of industrial processes).

Environmental Assessment

CSTL projects related to the assessment of environmental health cover a wide range, including the development of methods to measure pollutants, the monitoring of atmospheric and marine environments, the compilation of reference data and certification of reference materials for use in environmental measurements, and the accreditation of commercial water testing laboratories.

NIST scientists collect sediment from the Buffalo River in the development of SRM 2704



Commercial Laboratory Proficiency Testing (PT) Studies **R.M. Parris, W.E. May (839), and C.D. Faison (TS)**

The Analytical Chemistry Division and National Voluntary Laboratory Accreditation Program have completed the first year of this program that was designed to provide a system under which private sector companies and state laboratories are accredited by NIST to provide proficiency testing that meets the needs of the Environmental Protection Agency and states for regulated chemical, microbial, and radiochemical parameters. In our role of developing and managing the program for chemical and microbial species, Standard Reference Materials have been established and maintained to support the program, and we have conducted blind sample audits of PT samples on an ongoing basis for the 12 currently accredited providers covering all 48 chemistry and microbiology PT program fields.

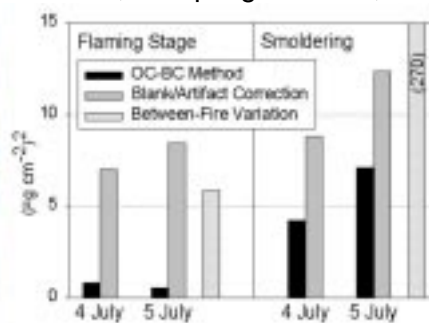


Sampling and Measurement of Atmospheric Aerosol Carbon from Forest Fires

J.M. Conny, G.A. Klouda (837), and J.F. Slater (University of New Hampshire)

Agricultural burning and wildfire activity are major sources of atmospheric aerosols that adversely affect global climate, health, and visibility. The chemical characterization of particles from burning is essential for assessing its contribution in ambient air and, in turn, for predicting the health and environmental effects of unabated burning. Due to emission variation, sampling artifacts, and

measurement method differences, fundamental challenges exist in determining the carbon composition of aerosols that accurately represent large-scale vegetative burning. The Surface and Microanalysis Science Division has been developing a procedure that uses the thermo-optical method, which involves the absorption of



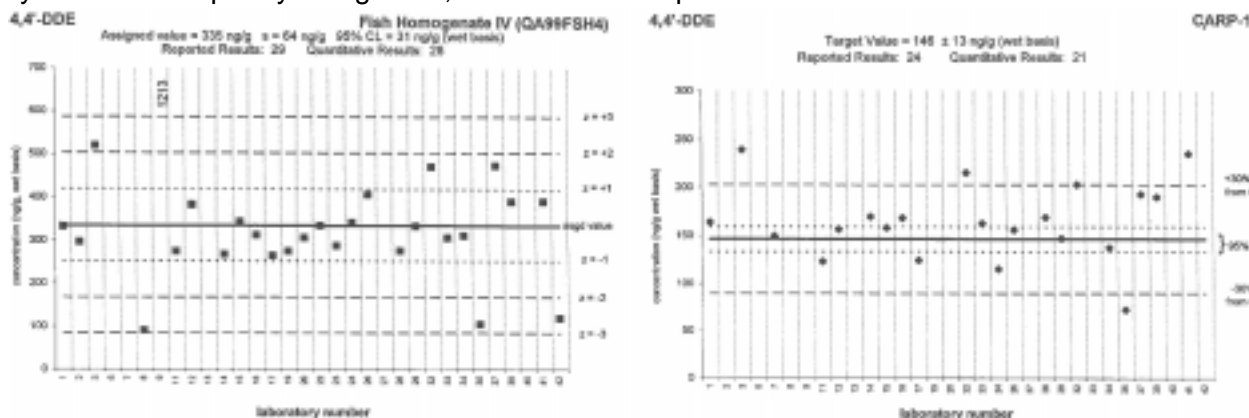
At left, aerosol sampling during flaming (arrow points to sampler)
At right, differences in collected aerosol particles from flaming and smoldering fire conditions

laser radiation by filter-collected aerosol particles at varying temperatures, to improve the accuracy and uncertainty in the measurement of the black carbon to total carbon ratio. This ratio is of great significance in parameterizing climate change models that relate to global warming.

Measurement Quality Assurance for Contaminants in the Marine Environment

M.M. Schantz, R.M. Parris, and S.A. Wise (839)

For over a decade, in collaboration with the National Oceanic and Atmospheric Administration's National Status and Trends Program, the Analytical Chemistry Division has coordinated annual intercomparison exercises for the measurement of polycyclic aromatic hydrocarbons, polychlorinated biphenyl congeners, and chlorinated pesticides in marine tissue and sediment to



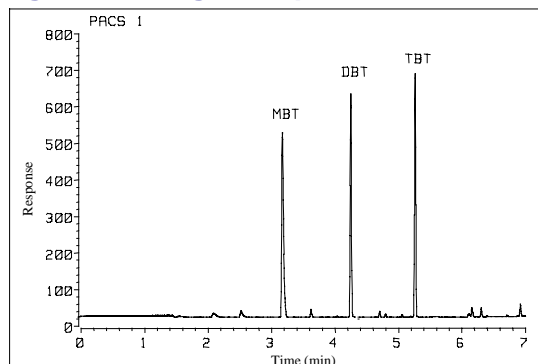
Shown above are the results for 4,4'-DDE from 42 laboratories in the 1999 exercise in which Fish Homogenate IV (candidate NIST SRM 1946) and Marine Sediment IX (candidate NIST SRM 1941b) were distributed

assess the comparability of analytical measurements among members of the marine environmental measurement community. Current participants include 42 federal, state/municipal, university/college, private sector, and international laboratories. The data received are combined to provide an assigned value for the unknown used in the exercise. Participation in the program is written into a number of federal government solicitations, including at least one Mineral Management Service and eight U.S. Environmental Protection Agency solicitations in the last year.

New Analytical Methodologies for Environmentally Significant Organic Species

***M.M. Schantz, D. Bezabeh, W.W. Brubaker, Jr.,
J. R. Kucklick, S. Tutschku, and S.A. Wise (839)***

Gas and liquid chromatographic methodologies are being developed for the quantification of organotins, dibenzo-*p*-dioxin (PCDD) and dibenzofuran (PCDF) congeners, polychlorinated naphthalenes (PCN), and nitro-substituted polycyclic aromatic hydrocarbons (nitro-PAHs) in natural matrices. These highly toxic substances have been measured in a number of SRMs with some verification through interlaboratory studies coordinated jointly by NIST and Environment Canada.



A typical chromatogram for the measurement of organotin species in SRMs using solid-phase microextraction – gas chromatography with atomic emission detection

NIST Traceable Reference Materials (NTRM™) from Commercial Sources

W.E. May, F. Guenther, W. Dorko, G.W. Kramer, J.C. Travis, G. Turk, J. Fassett, and R. Greenberg (839)



NTRMs are reference materials that have a well-defined traceability linkage to NIST that has been established using criteria and protocols defined by NIST and tailored to meet the needs of the metrological community to be served. Formal programs have been established to facilitate the commercial production and distribution of these materials in the areas of gas mixtures and optical filter standards, and programs for elemental solution and metal alloy standards are in the planning stages. Many of these materials, particularly pollutant gases and toxic element solutions, are critical for quality assurance of environmental measurements, and the increased availability of reference materials with a well-defined traceability linkage resulting from NTRM programs in these areas will significantly benefit our customers.

Aqueous-Phase Atmospheric Chemistry of the Nitrate Radical

P. Neta, G.A. Poskrebyshv, and R.E. Huie (838)

The behavior of the nitrate radical, NO_3 , is being studied to establish its role in the chemistry of the aqueous phase of the atmosphere. NO_3 , which is formed through the interaction of NO_2 and O_3 , is the most important free radical in the atmosphere at night, and is a critical component to atmospheric chemistry models. Since there is great difficulty in generating NO_3 in aqueous solution, laboratory results of reactivity studies are often discordant. This study has provided reliable values for rate constants of reactions critical to atmospheric chemistry.

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Reference Methods and Standards for Environmentally-Significant Inorganic Species

R.R. Greenberg, R. Demiralp, W.R. Kelly, R.M. Lindstrom, S.E. Long, and R. Zeisler (839)

Environmental monitoring and research programs are being supported through the development of analytical methods and SRMs. A primary example is the development of ICP-MS and RNAA methods for mercury that has led to the certification of the mercury concentration in SRM 1632c (Bituminous Coal). The improved accuracy and precision of the NIST methods have resulted in SRMs that provide traceability for power industry measurements of mercury. The Environmental Protection Agency (EPA) has stated that mercury is the top priority elemental pollutant in the environment, but in recent years no SRMs have been available to provide the traceability for power industry measurements due to the difficulty in making accurate and precise low-level determinations of mercury in a coal matrix. The Electric Power Research Institute (EPRI) has been conducting a round-robin study to assess the status of the most commonly used industry methods for mercury in coal, but the lack of a reliably certified coal SRM has initially limited the assessment of data accuracy. The improved accuracy and precision (method agreement was within ~1%) of the NIST methods will alleviate these problems as well as facilitate reliable long-term stability testing of SRMs certified for mercury.

The improved accuracy and precision of the NIST methods have resulted in SRMs that provide traceability for power industry measurements of mercury.

Structure, Adsorptive Separations, and Characterization of Surfactant/Clay Complexes

C.D. Muzny, T.J. Bruno, and H.J.M. Hanley (838)

Clay is a key inorganic substance in a broad array of applications ranging from pollution prevention and remediation, enhanced oil recovery, the treatment of petroleum liquids, the manufacture of cosmetics and pharmaceuticals, and the synthesis of polymer nanocomposite materials. An understanding of clay-organic chemical interactions and the effects these interactions have on the structure of clay complexes is a critical issue for future developments in all of these applications. Characterization of structural changes induced in polymer-clay

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nanocomposite materials by variation of the organic clay surface modification is being examined by small-angle neutron scattering (SANS), wide-angle x-ray scattering (WAXS), and dynamic light scattering (DLS), to permit correlation of small-scale structural changes with macroscopic property changes. In addition, advances were made in physicochemical gas chromatography by devising stable clay- and organoclay-coated capillary columns to study the chemical kinetics of the clay-organic interactions. The capillary column approach is more efficient, requires lower column temperatures, and produces values of the enthalpy of adsorption (H_{ads}) with a much lower uncertainty than conventional techniques. The scattering results have provided evidence that

complete exfoliation of clay particles in a polymer matrix is very difficult to achieve. When nanocomposite materials were produced from well-dispersed organoclay solutions, an apparent flocculation transition was observed during polymerization preventing the complete dispersion of the clay in the polymer matrix. Future plans are to combine computer simulation techniques with the results of the scattering investigations in order to accurately model the local structures present in clay solutions and nanocomposite materials, and to coordinate structure surface studies with thermodynamic information obtained from the coated capillary column. In addition, we have begun extending the chromatographic technique to the measurement of the diffusion of pollutants into the clay and organoclay system.

A Primary Reference Photometer for Ozone Measurements

P.M. Chu, J.E. Norris, and F.R. Guenther (839)

In partnership with researchers at the Bureau International des Poids et Mesures (BIPM), the Analytical Chemistry Division is developing an advanced primary ozone photometer with improved SI-traceability to assure the comparability and SI-traceability of global ozone measurements. The new instrument will allow for optical probes at multiple wavelengths rather than at a single Hg line, so that ozone, nitrogen dioxide, nitric oxide concentrations and other contaminants can be measured simultaneously.



Viewing the Absorption Cells of the Standard Reference Ozone Photometer

Gas Sensing with Microhotplate Sensor Arrays

R. Cavicchi, S. Semancik, C. Wheeler, J. Allen, J. Tiffany, M. Carrier, J. Melvin (836) J. Suehle (EEEL) D. DeVoe, and B. Panchapakesan (University of Maryland)

Details provided in the **Chemical and Biochemical Sensing** section.

Development of Optical Methods for Chemical Sensing

A.C.R. Pipino, J.T. Hodges (836) D.J. Vanderah, and C.W. Muese (831)

Details provided in the **Chemical and Biochemical Sensing** section.

National Particulate Matter Research Program

R.M. Verkouteren, G.A. Klouda, R.A. Fletcher, J.A. Small (837), J.R. Sieber, R.L. Zeisler, S.A. Wise (839), and J.M. Ondov (University of Maryland)



New Standard Reference Material for Air-borne Particulate Concentrations (SRM 2784 Urban Dust On Quartz Filters)

As a consequence of increased interest in atmospheric particulate matter (PM) research that resulted from the 1997 revisions to the National Ambient Air Quality Standards designed by the EPA, the Analytical Chemistry Division and the Surface and Microanalysis Science Division of NIST along with the University of Maryland have generated proposals to address measurement issues. This has resulted in an interagency agreement between EPA and NIST to 1) develop an urban PM-on-filter reference material for carbonaceous species; 2) develop methods and metrology needed to provide PM calibration materials for organic and elemental carbon analysis; 3) develop a special thin-film glass standard for X-ray fluorescence analysis; 4) develop technology for large scale collection of air particulate matter less than 2.5 micrometers in diameter (for subsequent SRM development); and 5) develop a modern bulk urban dust material (and soluble extracts) with reference values for selected organic constituents.

Quantitative Infrared Database Developed to Support Remote Sensing Applications

P.M. Chu, F.R. Guenther, G.C. Rhoderick, and P.A. Johnson (839)

NIST Standard Reference Database 79 (SRD 79) "Quantitative Infrared Database" is being developed to support optical-based measurements of chemical emissions and hazardous air pollutants (HAP). Currently, absorption coefficient data for 30 HAPs on the U.S. EPA priority list is available in the standard JCAMP-DX format to enable universal access to the data. Future direction for the project will involve continued data acquisition for compounds listed in the 1990 US EPA Clean Air Act Amendment, as well as for those compounds that are of concern in global warming and emissions trading. Additionally, intercomparisons of NIST primary standards and molar absorptivity data with other National Metrology Institute's data will be expanded to facilitate the use of this database in issues of global interest and impact.



Green Chemistry

CSTL projects related to Green Chemistry result from our mission as the Nation's Reference Laboratory to provide the chemical measurement infrastructure to both enhance U.S. industry's productivity and competitiveness, and to improve environmental quality. Towards that shared goal, the projects described below involve the development of innovative procedures and reference materials and the compilation of critical data that will significantly improve efficiency and reduce waste in industrial processes.

Standards to Assist Perfluorocarbon Reductions in Aluminum Production

G.C. Rhoderick, P.M. Chu, and F.R. Guenther (839)



The Analytical Chemistry Division is helping the Voluntary Aluminum Industrial Partnership (VAIP) to reduce emissions of perfluorinated carbon compounds (PFCs) and greenhouse gases and improve the efficiency of aluminum production through the development of a suite of eight primary gas standards for CF_4 and C_2F_6 . The development of these transfer PFC gas standards has assisted the aluminum industry in establishing traceability and mutual confidence in data generated for PFC emissions.

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The improved accuracy of measurements resulting from these standards has permitted better understanding and control of the "anode effects" that cause the production of PFCs, and in 1999 the VAIP reported reductions in PFC emissions by 41 %, equivalent to a reduction of nearly 8 million metric tons of CO_2 , from 1990 levels.



Atmospheric Lifetimes, OH Kinetics, and UV Spectra of Bromine-Substituted Fluoroalkenes

V.L. Orkin, F. Louis, M.J. Kurylo, and R.E. Huie (838)

Details provided in the **Chemical and Biochemical Data** section.

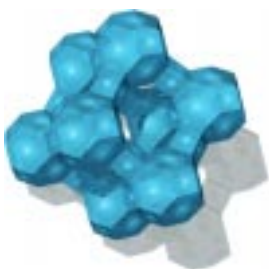
Application of Process Models and Controllers to Semiconductor Processing

R. W. Davis, J. E. Maslar, E. F. Moore (836), D. R. Burgess, Jr. (838), R. L. Axelbaum (Washington University), and S. H. Ehrman (University of Maryland)

Details provided in the **Microelectronics** section.

Reference Standards for Zeolites

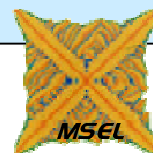
J.R. Sieber, T. W. Vetter, T.F. Marlow, R.L. Zeisler (839), and S. Turner (837)



Zeolites are environmentally friendly: non-hazardous, regenerable, and non-corrosive. Zeolite catalysts are widely used in industry, but the characterization of zeolite composition is critical since variations in silica-to-alumina ratios, pore sizes, surface area, cations, and incorporated metals produce a wide range of adsorbent and catalytic properties. The need for zeolite reference materials was identified at a National Science Foundation sponsored workshop with participants from the research community, users, and suppliers. The lack of common materials for comparative measurements was identified as an important barrier to the development of

new materials. These SRMs will provide a basic set of zeolite types to benchmark physical and chemical measurements. Chemical composition measurements for these standards were made in the Analytical Chemistry Division using X-ray Fluorescence Spectrometry, and nuclear and classical methods. The physical parameters (particle size and lattice parameters) were measured in the Surface and Microanalysis Science Division, which championed this project, and the Materials Science and Engineering Laboratory.

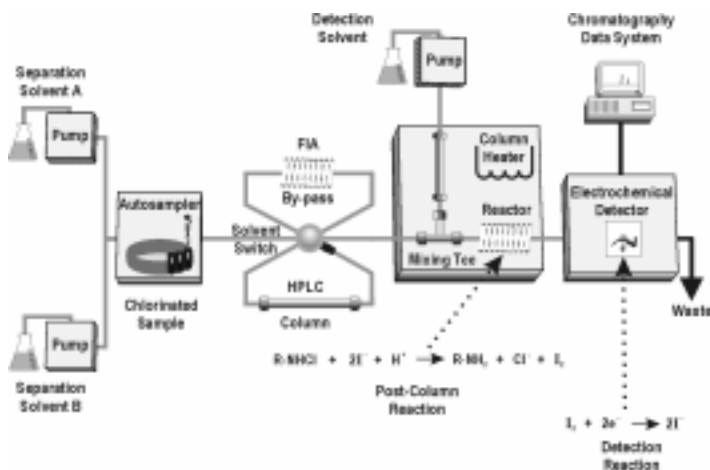
Zeolite Standard Reference Materials (SRMs) have been developed for use in the minimization of pollution and the treatment of effluents in industrial processes.



Wastewater Chlorination/Dechlorination Mechanisms

W.A. MacCrehan, M. Bedner (839), and G. Helz (University of Maryland)

To support national initiatives in developing environmentally-friendly, "green" chemical processing, the Analytical Chemistry Division is collaborating with the Water Resources Center of the University of Maryland to investigate new wastewater processing chemistries. The work is directed towards understanding and controlling chlorination residuals by developing a reliable measurement tool, liquid chromatography with post-column electrochemical detection, which can speciate the various forms of active residual chlorine. By understanding how the various chlorine species behave in their reaction with dechlorination agents, we hope to help sewage process engineers minimize the amount of wastewater chlorination by-products discharged into the environment.



A schematic diagram of the separation system designed to toggle between a flow injection analysis (FIA) (with no separation column) and the liquid chromatographic (LC) separation, permitting the direct evaluation of the factors that influence on-column losses such as solvent composition, pH, and separation column material

Detoxification of Polychlorinated Compounds in Water, Oil, and Soil by Electron Beam Irradiation

D.L. Poster (839), R.E. Huie, P. Neta (838), M. Chaychian, C. Jones, J. Silverman, and M. Al-Sheikhly (University of Maryland)

The radiolytic degradation of PCBs present in contaminated matrices is being examined to evaluate techniques that increase the efficiency of PCB dechlorination. Methods include using non-toxic additives, surfactants, and sonication during the electron beam treatment, using additives (alcohol, alkali) and applying an external high voltage electric field during electron beam irradiation in transformer oil, as well as evaluating the cost and performance of radiolytic treatment methodologies for the remediation of the most prevalent types of PCB contamination at polluted sites. One hundred percent dechlorination of PCBs in BG&G transformer oil has been achieved using electron irradiation and added triethylamine.

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Thermodynamic Data for Aqueous Terrestrial Processes at Subfreezing Temperatures

D.G. Archer and R.W. Carter (838)

Details provided in the **Physical Property Data** section.

Properties of Lubricants and Lubricant/Refrigerant Blends

M. Huber, T. Bruno (838), K. Henning, M. Spadi (Institute Louis Pasteur, France), A. Abdulagotov (Dagestan Scientific Center of Russian Academy of Sciences), and M. Killeen (Guest Researcher)

Details provided in the **Physical Property Data** section.

Biocatalytic Systems

W.M. Byrnes, D.T. Gallagher, M.J. Holden, M.P. Mayhew, A.E. Roitberg, B. Coxon, and V.L. Vilker (831)

Details provided in the **Bio-Molecules and Materials** section.